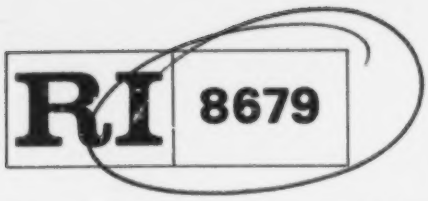

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Hydrometallurgical Treatment of Arsenic-Containing Lead-Smelter Flue Dust

By P. A. Bloom, J. H. Maysilles, and H. Dolezal

UNITED STATES DEPARTMENT OF THE INTERIOR

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HYDROMETALLURGICAL TREATMENT OF ARSENIC-CONTAINING LEAD-SMELTER FLUE DUST

By P. A. Bloom,[1] J. H. Maysilles,[2] and H. Dolezal[3]

ABSTRACT

Arsenic-containing flue dusts are currently being stockpiled by several nonferrous smelters in the United States. These stockpiles are a source of environmental concern since the dusts can be transported by wind and contain water-soluble arsenic. The stockpiles also represent an alternate source of metals. To provide a quality environment, the Bureau of Mines investigated a process to make environmentally acceptable the discard of arsenic obtained from the treatment of arsenical flue dust.

The process includes (1) leaching arsenic from a lead smelter copper dross flue dust, (2) fixing arsenic as an insoluble compound, and (3) recovering other metal values. Overall results of acid-leaching tests on lead-smelter flue dusts showed that H_2SO_4 dissolved 80 to 90 percent of the As, Zn, and Cd, and up to 86 percent of the In. Pb, Ag, and Au remain in the residue, which can be recycled to the smelter. Indium was recovered from the strong acid leach solution by solvent extraction; arsenic was fixed in a stable form by precipitation with $Fe_2(SO_4)_3$ and CaO or $CaCO_3$.

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INTRODUCTION

Raw materials processed in lead and copper smelting operations contain toxic elements, usually arsenic. This element cannot be tolerated in the final metal product and must be disposed of as a byproduct or waste. One U.S. lead smelter produces a flue dust containing 10 percent arsenic in the drossing operation. Removal of the dust prevents the buildup of arsenic that would occur if it were recycled to the smelter. It is currently being stockpiled pending development of processing technology. Several thousand tons of stockpiled material are a potential environmental hazard. The dust could be dispersed by wind if it were not kept wetted down, and since it contains water-soluble arsenic, there is danger that it may pollute ground water. Similar stockpiles exist at other western copper smelters where recyling of dust causes a buildup of arsenic in reverberatory smelting operations that must be bled off. Therefore, it is highly desirable to chemically and/or physically convert this toxic material to a stable form.

Arsenic-containing flue dust might be prevented from contacting the environment by three methods: (1) Removing arsenic from smelter feed materials, resulting in less toxic dust, (2) mixing the dust with wet concrete or molten slag to fix the arsenic, or (3) recovering or fixing arsenic as a step in recovering major and minor metal components.

The first approach may be impractical because of the volume of material processed. The lead smelter producing arsenic-containing dust processes about 500 tons of concentrate per ton of dust generated. The existing stockpile must still be treated. The second approach seems technologically possible, and significant research in this area has already been done (3).[4] However, this method would be wasteful since all metal values in the dust would be lost. The third approach is the most satisfactory solution to the problem; since it combines recovery of metal values from flue dust with separation of arsenic as a product or a stable disposable material.

A research objective of the Salt Lake City Research Center was the development of hydrometallurgical processes for removing arsenic from flue dusts and related materials so these materials could be treated later for metal recovery. For example, lead smelter flue dust contains large fractions of lead and zinc, which are reclaimable by hydrometallurgical treatment. Zinc can be solubilized, and the lead-enriched residue can be returned to the smelter.

The recovery of valuable minor components from flue dust is a logical extension of the above research. Some elements, including indium recovered in the smelting operation, appear in relatively high concentrations in process byproducts. Once process flowsheets are developed for separation of arsenic and recovery of metals comprising the bulk of the dust, the behavior of these minor components can be determined, and process modifications for their recovery can be explored. Thus, the Bureau of Mines investigated (1) the recovery of byproduct metals from flue dust, which would help meet its goals of fully utilizing the Nation's mineral resources and developing alternative sources of scarce metals, and (2) methods for fixing arsenical wastes in an environmentally safe form. This report covers experiments performed with arsenical dust samples from a lead smelter.

The technology developed was best suited for what was then an existing lead smelter with an adjoining electrolytic zinc plant. This smelter is no longer operating, but large stockpiles of arsenical flue dust are still at the site which will have to be disposed of,

[4]Underlined numbers in parentheses refer to the items in the list of references at the end of this report.

treated in place, or shipped to an outside processor. The processing steps investigated can be applied to the treatment of this dust and to similar dusts from other lead or copper smelters.

DESCRIPTION OF THE SAMPLES

Three dust samples were obtained from a lead smelter for experimental work. Analyses of these samples and their designations are shown in table 1. Sample 1 was taken from a composite, supposedly representative of the stockpile. Dry dust (sample 2) was taken directly from the drossing operation. Sample 3, a grab sample of the stockpile, contained more zinc than the composite sample.

TABLE 1. - Assays of lead smelter flue dust samples

Sample	Description	Assay, wt-pct										
		As	Pb	Zn	Cd	Sb	In	Cu	Fe	Ag[1]	SO_4^{2-}	Cl^-
1.....	Composite sample....	10.0	41.0	10.3	0.79	3.5	0.26	0.10	0.28	2.9	7.0	0.14
2.....	Dry sample.....	10.0	51.0	16.2	.22	1.4	.36	.16	.03	5.0	6.9	-
3.....	High-zinc sample[2]...	7.0	45.0	21.0	.20	2.4	.55	.21	.40	3.9	9.8	.25

[1]Assays in troy ounces per ton.
[2]Grab sample from stockpile.

Physically, all three samples consisted of very finely divided material. Sample 1 was 85 weight-percent minus 400 mesh and 25 percent minus 20 micrometers. A few physical beneficiation tests were conducted to see if it could be concentrated by screening, flotation, or tabling, but no significant separations of As, Pb, or Zn resulted. Physical separation methods were not effective for this material because there was a large fraction of fines.

EXPERIMENTAL STUDIES

Extensive bench-scale test work was done on the dust samples. The objectives were to separate arsenic as either a usable product or a stable reject, recovering as much of the metal values in the dust as feasible. Throwaway products and process effluents were evaluated from an environmental standpoint.

Lead-zinc smelting plants already recover Pb, Zn, Cd, and Ag. The possibility was considered of integrating an arsenic removal scheme by recycling arsenic-free dust or its components to existing facilities. A smelter was contacted to find out what dust elements must be removed before the remainder can be added to the smelter feed. Their criterion was that the dust can be recycled if a minimum of 75 percent of the arsenic is removed.

A hydrometallurgical testing program began for treating the flue dust samples by the following general scheme: (1) Preleach treatment (if necessary), (2) arsenic separation by leaching, (3) arsenic removal and recovery of values from solution, and (4) recovery of values from leach residue. A composite dust sample (sample 1), representing the stockpile was used in most of the experimentation. Parallel tests were made on the other samples to determine if similar results would be obtained. The differences in the sample assays showed that some variation in the stockpile composition could be expected; therefore, allowances in methods were made.

Arsenic Removal by H_2SO_4 Leaching

Sulfuric acid leaching tests were all conducted in beakers with agitation provided by a two-bladed impeller with a 45° pitch. Impeller speed was fast enough to maintain the solids in suspension. The leach time for ambient temperature tests was determined from the start of agitation. In tests using elevated temperatures, leach time was arbitrarily determined from the time the slurry reached the desired temperature. Agitation was maintained during the warmup period. In leaches carried out at 90° to 95° C, warmup periods were up to one-half hour. At the end of the leach period, solids were separated from the leachate by vacuum filtration. Wash liquid was combined with the leachate and included as a portion of the pregnant liquor. Preliminary results showed that selective leaching of arsenic was not possible in an acid system. As, Zn, Cd, and In were solubilized together, leaving Pb and Ag in the residue. These preliminary results indicated that schemes needed to be developed to separate dissolved elements.

Extraction of As, Zn, Cd, and In by H_2SO_4 Leaching

Tests were conducted on the flue dusts to determine the effect on arsenic dissolution of such parameters as percent solids, residence time, temperature, and H_2SO_4 strength. Other factors considered were preleach treatment, including pugging or pelletizing and baking. Owing to the limited size of the samples available, parameters for all dusts were not established. However, test results presented in this paper indicate that the response of the three dusts to the treatment was the same.

Figures 1 and 2 illustrate the results of acid leaching the three dusts at various percent solids in an initial acid concentration of 10 percent H_2SO_4. Decreasing the solids-to-liquid ratio increased the dissolution of all values. The amount of As, Zn, and Cd dissolved in all three dusts increased markedly as the solids decreased to 15 percent, and further reduction to 5 percent increased As dissolution from 3 to 8 percent more. Indium solubility showed a markedly linear increase with decreasing solids-to-liquid ratio.

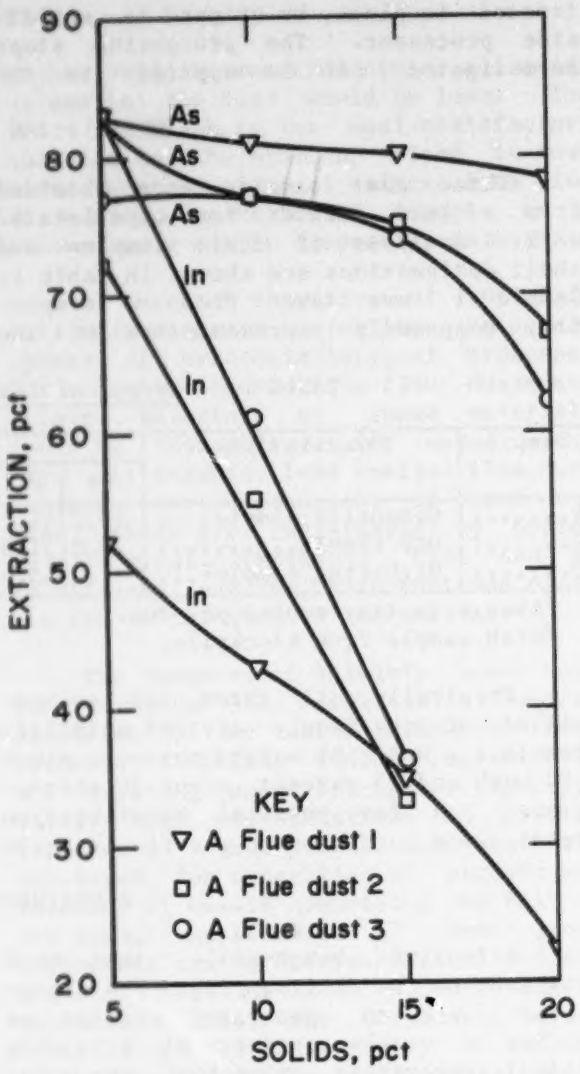

FIGURE 1. - Effect of percent solids on extraction of arsenic and indium leached 4 hours with 10-percent H_2SO_4 at ambient temperature.

The effect of time on the leaching operation was tested on samples 1 and 3 by varying contact time from 10 to 240 minutes. All tests were made using 10 percent solids in an initial acid

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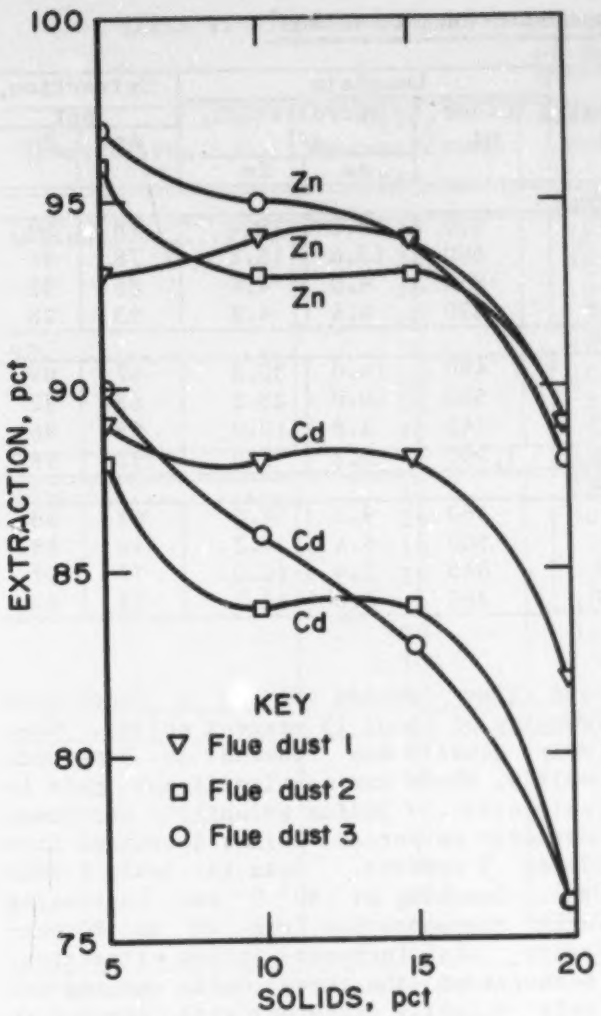

FIGURE 2. - Effect of percent solids on extraction of zinc and cadmium leached 4 hours with 10-percent H_2SO_4 at ambient temperature.

concentration of 20 percent H_2SO_4. The results are listed in table 2. The dissolution of the As, Zn, Cd, and In compounds in H_2SO_4 did not require more than 10 minutes; however, greater contact time was deemed necessary for test purposes to assure completion of reactions.

TABLE 2. - Effect of time on extraction

Leach time, min	Extraction, pct			
	As	Zn	Cd	In
SAMPLE 1				
10.....	86	89	84	51
30.....	84	90	81	53
60.....	86	91	85	56
240.....	84	93	83	56
SAMPLE 3				
10.....	82	97	83	76
30.....	83	97	83	79
60.....	82	98	84	81
240.....	71	95	86	61

The effect of temperature on the extraction of arsenic and zinc at ambient temperatures and 90° C was determined in one test series on two levels of solids content, 5 and 20 percent, using an initial acid concentration of 10 percent H_2SO_4 and a 4-hour leaching time. The results of these tests are shown in table 3. In these tests the zinc extraction either was steady or improved with temperature. Arsenic extraction from a leach containing 5 percent solids was also improved by increasing the temperature. However, arsenic extractions tended to drop off at 90° C in leaches containing 20 percent solids. This decrease in extraction may be caused by an increased amount of lead in the residue being converted to sulfate and depleting the acid strength. This effect is confirmed by the data in table 3, which show increases in pH and a trend toward decreasing arsenic extraction for leaches made with 20 percent solids at 90° C.

TABLE 3. - Effect of temperature on extraction[1]

Temperature, ° C	Solids, pct	Final pH	Leachate			Extraction, pct	
			Volume, ml	Concentration, g/l		As	Zn
				As	Zn		
SAMPLE 1							
Ambient	20	0.8	500	14.2	19.4	78	89
90	20	1.2	600	13.6	16.2	78	96
Ambient	5	.43	850	4.0	4.8	86	92
90	5	.48	830	4.4	4.8	93	98
SAMPLE 2							
Ambient	20	1.4	480	14.0	30.2	67	89
90	20	1.7	580	10.8	25.2	65	92
Ambient	5	.42	760	3.8	10.0	83	96
90	5	.40	1,000	3.2	7.0	92	98
SAMPLE 3							
Ambient	20	1.6	460	9.2	38.0	52	88
90	20	2.1	500	6.4	37.2	46	88
Ambient	5	.64	845	2.4	10.0	77	97
90	5	.37	760	2.6	12.2	78	97

[1]4-hour leach with 10-percent H_2SO_4.

In another test series, also of 4-hour duration at ambient temperatures and at 90° C, two levels of solids in a lower percentage range were used, 5 and 10 percent, together with two levels of initial acid concentration, 10 and 20 percent H_2SO_4. The results for these tests, presented in table 4, show that arsenic extraction can be enhanced both by increased acid concentration and by increased temperature. In this series of tests, a decrease in arsenic extraction with increased temperature was avoided because the pulp density was kept below 20 percent.

In summary, results for H_2SO_4 leaching tests on smelter flue dust presented in figures 1 and 2 show that in addition to As, a large amount of Zn was leached along with significant amounts of Cd and In. In general, conditions favoring As dissolution also favored dissolution of Zn, Cd, and In. Solubilities of cadmium and zinc leveled off at a leach-pulp density of about 15 percent solids. When pulp density was reduced to 5 percent solids, there was no significant gain in extraction. Indium solubility increased markedly as percent solids decreased from 15 to 5 percent. Data in table 4 show that leaching at 90° C and increasing acid concentration from 10 to 20 percent. also increases indium extraction. Behavior of the three dust samples was only slightly different with respect to acid concentration, percent solids, and temperature. Zinc extracted well (over 90 percent) under all the conditions, and cadmium followed the behavior of zinc. In general, higher acid concentration and temperature increased zinc solubility slightly and increased cadmium solubility about 4 to 5 percent. The operation was complicated by leaching of Zn, Cd, and In along with As, and there was no way of efficiently leaching these elements selectively.

TABLE 4. - Effect of acid concentration and temperature on extraction of As, Zn, Cd, and In[1]

Temperature, ° C	H_2SO_4 concentration, pct	Solids, pct	Leachate concentration, g/l				Extraction, pct			
			As	Zn	Cd	In	As	Zn	Cd	In
SAMPLE 1										
Ambient	10	10	9.0	10.8	0.77	0.12	81	94	88	43
	20	10	9.2	10.6	.73	.16	84	93	83	56
	10	5	4.4	5.0	.37	.07	83	93	89	52
	20	5	4.2	5.2	.36	.09	90	96	86	67
90	10	10	9.7	11.3	.80	.18	87	99	92	47
	20	10	.2	11.1	.80	.18	92	97	91	64
	10	5	4.9	5.3	.37	.08	93	98	89	57
	20	5	4.9	5.3	.39	.11	94	98	94	80
SAMPLE 2										
Ambient	10	10	8.5	16.7	0.21	0.22	77	93	84	55
	20	10	9.2	16.9	.20	.29	83	94	83	72
	10	5	4.4	8.2	.11	.14	86	96	91	72
	20	5	4.4	8.3	.10	.16	84	97	86	84
90	10	10	9.4	17.3	.20	.21	85	96	89	53
	20	10	9.7	17.5	.22	.30	87	97	89	75
	10	5	4.7	8.4	.11	.14	89	98	93	74
	20	5	4.7	8.4	.11	.16	89	98	93	86
SAMPLE 3										
Ambient	10	10	6.0	22.2	0.19	0.37	77	95	86	61
	20	10	6.0	22.2	.18	.48	77	95	83	78
	10	5	2.8	10.7	.09	.24	77	97	90	83
	20	5	2.9	10.8	.09	.23	80	98	89	79
90	10	10	5.4	21.9	.19	.41	70	94	87	67
	20	10	6.0	22.2	.19	.49	77	96	84	80
	10	5	2.9	10.7	.09	.23	76	97	86	81
	20	5	3.1	10.8	.10	.23	83	98	91	80

[1]Leaches were of 4-hour duration.

Extraction of As, Zn, Cd, and In by Pugging or Pelletizing, Roasting, and Leaching

The effect of increasing acid strength and temperature for arsenic extraction was examined by pugging or pelletizing the dust with sulfuric acid, roasting, and water leaching.

The dust was pugged with either concentrated or 70 volume-percent H_2SO_4. The acid was mixed with the dust until the dust was thoroughly blended. The pugged mixture was roasted for 4 hours at 175° C in a muffle furnace. The roast product was pulped to a density of 20 percent solids in 10 weight-percent H_2SO_4 and leached for 1 hour at ambient temperature.

Pelletizing the flue dust was accomplished in a 5.5-inch-tall, 6-inch-diameter drum. The speed of the cylinder had to be fast enough to get a good rolling action and was left to the judgment of the operator. After pelletizing with concentrated H_2SO_4, the dust was handled the same way as described for the pugging process.

Pugging and pelletizing tests were confined to the sample 3 dust. Acid additions were limited by the amount of liquid needed for agglomeration; consequently the pellets contained less H_2SO_4 than pugged samples.

The results of these tests are shown in table 5. Baking preceded by pugging or pelletizing does not appear to have any advantage over conventional acid agitation leaching.

TABLE 5. - Comparison of extraction results obtained by leaching, pugging-baking-leaching, or pelletizing-baking-leaching

Treatment	Extraction, pct			
	As	Zn	Cd	In
Agitation leaching.....	77.0	96.0	84.0	80.0
Pugging-baking-leaching.....	75.0	97.9	83.0	78.0
Pelletizing-baking-leaching.....	64.0	NA	NA	NA

NA Not analyzed.

Recovery of As, Zn, Cd, and In From Leach Solutions

Leach solutions from the lead smelter flue dust contained, in grams per liter, 5 to 20 As, 5 to 37 Zn, 0.1 to 0.8 Cd, and 0.1 to 0.5 In. It was decided that methods would be defined or developed for the recovery of marketable products from the Zn, Cd, and In, and that the arsenic would be precipitated in an environmentally safe form.

Selective Precipitation of Arsenic

Several additives were tested as reagents for selective precipitation of arsenic, including (1) ferric sulfate ($Fe_2(SO_4)_3$) with pH control, (2) calcined zinc concentrates, and (3) either hydrogen sulfide (H_2S), sodium sulfide (Na_2S), or sodium hydrosulfide (NaHS).

Unless the precipitate meets the Environmental Protection Agency (EPA) requirement for a nonhazardous solid waste (4, pp. 33127-33128), it must be disposed of in specially prepared sites. To meet the EPA requirement for a nonhazardous solid waste, the precipitate must pass a 24-hour agitation leach test made under the following conditions: Ambient temperature, pH of 5±0.2, and about 6 percent solids. The pH is maintained with additions of 0.5 N acetic acid. No acetic acid is added if the natural pH of the slurry is 5 or less. At the end of the leach period the slurry is diluted with water to equal 20 times the weight of the original dry solids, minus the water and acid used for leaching. The slurry is filtered. The arsenic content of the filtrate must not exceed 5 milligrams per liter (4, p. 33122) for the precipitate to be nonhazardous.

Precipitation of Arsenic With $Fe_2(SO_4)_3$ and pH Control

One of the simplest and most economically attractive methods for the removal of arsenic from solutions reported in the literature (2-3, 6) is by coprecipitation with ferric iron ($iron^{3+}$). This method is effective in removing both trivalent and pentavalent arsenic, but the mechanism by which it works has not been fully explained. Adsorption on ferric hydroxide $Fe(OH)_3$ and formation of ferric arsenates ($FeAsO_4$) and ferric arsenites ($2FeAsO_3 \cdot Fe_2O_3$) have both been proposed to explain what happens.

Coprecipitation tests were conducted on liquors obtained by leaching sample 1. In these tests, a $Fe_2(SO_4)_3$ solution was used as a source of iron, and pH was controlled with additions of either CaO, $CaCO_3$, Na_2CO_3, or NaOH. Table 6 gives data obtained on the effects of pH and the iron-arsenic mole ratio on the precipitation of arsenic and other elements.

Results show that selectivity for precipitation of arsenic is best in a pH range of 3.1 to 3.4 and at an iron-arsenic ratio above 1.2. The best overall precipitation of arsenic was obtained in a pair of similar tests using CaO and $CaCO_3$ for pH control; in these tests the respective percentages of As precipitated were 99.0 and 98.4, while the respective percentages of coprecipitates were 0.4 and 0.4 of Zn and 3.5 and 5.3 of Cd. One hundred percent of indium in solution was also precipitated in all tests. Raising the pH resulted in slightly more arsenic removal, but the amount of zinc and cadmium that coprecipitated also increased. At a pH of 4.0, 12 percent of zinc and 18 percent of cadmium in solution coprecipitated. The best results were obtained using either CaO or $CaCO_3$ for pH control; good results were also obtained with Na_2CO_3. Although Na_2CO_3 is more expensive, its use might be advantageous in some cases since the bulk of precipitate formed would be considerably less than when CaO or $CaCO_3$ are used. Other than cost, the main drawback to the use of Na_2CO_3 is the formation of Na_2SO_4, which is very soluble and presents a difficult disposal problem.

TABLE 6. - Precipitation of arsenic with ferric iron from acid leach liquors

Reagent for pH control	Final pH	Fe-As ratio[1]	Elements precipitated from solution, pct[2]		
			As	Zn	Cd
CaO.....	3.0	0.4	81.0	22.0	54.0
CaO.....	3.1	.5	86.0	13.0	38.0
CaO.....	4.0	1.5	99.8	12.0	18.0
CaO.....	5.3	1.0	99.8	30.0	60.0
CaO.....	3.4	1.7	99.0	.4	3.5
$CaCO_3$.....	3.1	1.7	98.4	.4	5.3
Na_2CO_3.....	3.0	1.7	93.0	4.6	5.4
NaOH.....	3.1	1.2	96.0	1.9	4.4

[1]Fe-As ratio indicates iron added to arsenic in solution on a mole ratio basis.

[2]All of the indium in the solution was precipitated.

Iron-arsenic precipitates prepared as described above contained 4.5 to 5.5 percent arsenic. Repeated tests of the iron-arsenic precipitate have shown that filtrates obtained by the EPA test procedure contain, in milligrams per liter, 1 to 4 of arsenic and about 40 to 50 of cadmium. Although the arsenic is safely fixed, the iron-arsenic precipitate will not meet EPA standards for a nonhazardous disposable product because of its soluble cadmium.

Precipitation of Arsenic With Calcined Zinc Concentrates

Calcined zinc concentrates were tried as an arsenic precipitant because they contained zinc oxide and zinc ferrite ($ZnFe_2O_4$). The use of zinc concentrates was based on the supposition that excess acidity would be neutralized by the zinc and that $Fe_2(SO_4)_3$ for precipitation of arsenic would become available by dissolution of $ZnFe_2O_4$. Actual tests showed that the calcine was not very reactive. When enough of the calcine was added to raise the leach solution pH to 3.0, 96 percent of the arsenic could be precipitated, leaving a solution that still contained 0.6 gram per liter of arsenic. However, because of its low reactivity, about 34 percent of the zinc in the calcine remained in the precipitate. It was concluded that this scheme was wasteful and costlier than the use of either CaO or $CaCO_3$.

Precipitation of Arsenic as a Sulfide

A few tests were made using either H_2S, Na_2S, or NaHS to precipitate arsenic

as a sulfide (As_2S_3 or As_2S_5). Results obtained with all of these reagents were similar. At a pH of 0.9 and a temperature of 90° C, almost 100 percent of the As was precipitated while over 99 percent of the Zn, Cd, and In remained in solution. At ambient temperatures, the results were quite different. Up to 72 percent of the As remained in solution while almost 50 percent of the Zn, Cd, and In coprecipitated with the arsenic. The sulfide precipitates were slimy and difficult to filter. No further work was done on this approach because of the poor handling characteristics of the arsenic sulfide precipitates.

Recovery of Zinc

After precipitation of the arsenic, the remaining solutions have zinc as the main solute with small amounts of cadmium and other elements not determined. Attempts to purify these solutions by pH control were not productive and were discontinued. The technology already in use by electrolytic zinc producers (5), which is based on cementation of impurities with zinc dust, is well known and can be used on these solutions. If the dust is treated at a lead smelter with an adjoining zinc electrowinning plant, the leach solution can be combined with zinc calcine and zinc metal can be produced. If the treatment is done at a remote site, the solution might be concentrated and a marketable $ZnSO_4$ product recovered by crystallization or spray drying.

Recovery of Cadmium

Results from tests on precipitation of arsenic with $Fe_2(SO_4)_3$ and CaO in table 6 showed that a small amount of cadmium tended to coprecipitate with the arsenic. At a pH of 3.4, using an iron-arsenic mole ratio of 1.7, about 3.5 percent of the cadmium in solution coprecipitated with the arsenic. However, this coprecipitation could not be made complete or selective. When the pH was raised to 5.3 and the iron-arsenic ratio was reduced to 1.0, 60 percent of the cadmium in the solution coprecipitated, but it also brought down 30 percent of the zinc. Decreasing the iron-arsenic ratio tended to increase the coprecipitation of cadmium more than raising the pH did, but it also increased the loss of zinc. Arsenic precipitate together with coprecipitated cadmium would be stockpiled. Cadmium remaining in solution after arsenic precipitation can be recovered by cementation on zinc powder in the manner used by electrolytic zinc producers (5) to purify their electrolytes.

Recovery of Indium

Leach solutions prepared with the higher acid strengths contained about 0.2 gram per liter indium, which would not stay in solution when the pH was raised above 2.0. Loss of all the indium could not be avoided when the pH was raised above 3.0 when the arsenic was precipitated. Attempts to selectively redissolve the arsenic or indium in the precipitate away from each other were unsuccessful. However, a method described in the literature (1) based on solvent extraction with di-(2-ethylhexyl) phosphoric acid (EHPA) was successfully tested. This solvent extraction method was very selective for removing indium from strong acid solutions, such as the leach liquors from flue dusts. Preliminary tests have shown that when an 0.2-gram-per-liter indium-leach solution was contacted with a 10-volume-percent solution of EHPA in kerosine, over 99 percent of the indium was extracted and the solvent was loaded to about 0.8 gram per liter indium. When the loaded solvent was stripped with 10-percent HCl or 5-percent HCl and 10-percent NaCl, with a strip-to-loaded organic ratio of 1:4, the concentration of indium in the strip liquor was about 3 grams per liter. Since indium can be recovered from solution by cementation, no other recovery methods were studied.

Recovery of Lead

Lead analysis of the the three dust samples ranged from of 41 to 51 percent. The lead contents were upgraded to a range of 51 to 64 percent by dissolving the arsenic and zinc. Most of the leach

residue was in the form of an insoluble lead sulfate ($PbSO_4$). A 51-percent-lead product is a little low for a sinter feed when compared with about 75 percent of lead concentrate. Even though lead sulfate is undesirable in lead concentrate smelting, the effect would be minimal because the amount of lead concentrate feed is very large compared with the small amount of leach residue produced. Sulfuric acid leach residues would also have all the precious metal content of the original dust, and these metals can be recovered with the lead when recycled.

DISCUSSION OF RESULTS

H_2SO_4 leaching of lead flue dust dissolved about 90 percent of the As, Zn, and Cd values. Successful leaching conditions, 90° C temperature, 20 percent H_2SO_4, and 5 percent solids, produced maximum amounts of dissolved As, Zn, Cd, and In. Indium solubility was especially sensitive to acid concentration and to pulp density. A proposed flowsheet for extraction is illustrated in figure 3. The flowsheet is based on the premises that the reclamation and disposal of the flue dust would take place in the proximity of a lead-zinc smelter, that lead-rich residue could be recovered by recycling to the lead blast furnace, and that the solutions could be used as makeup for the electrolytic zinc plant.

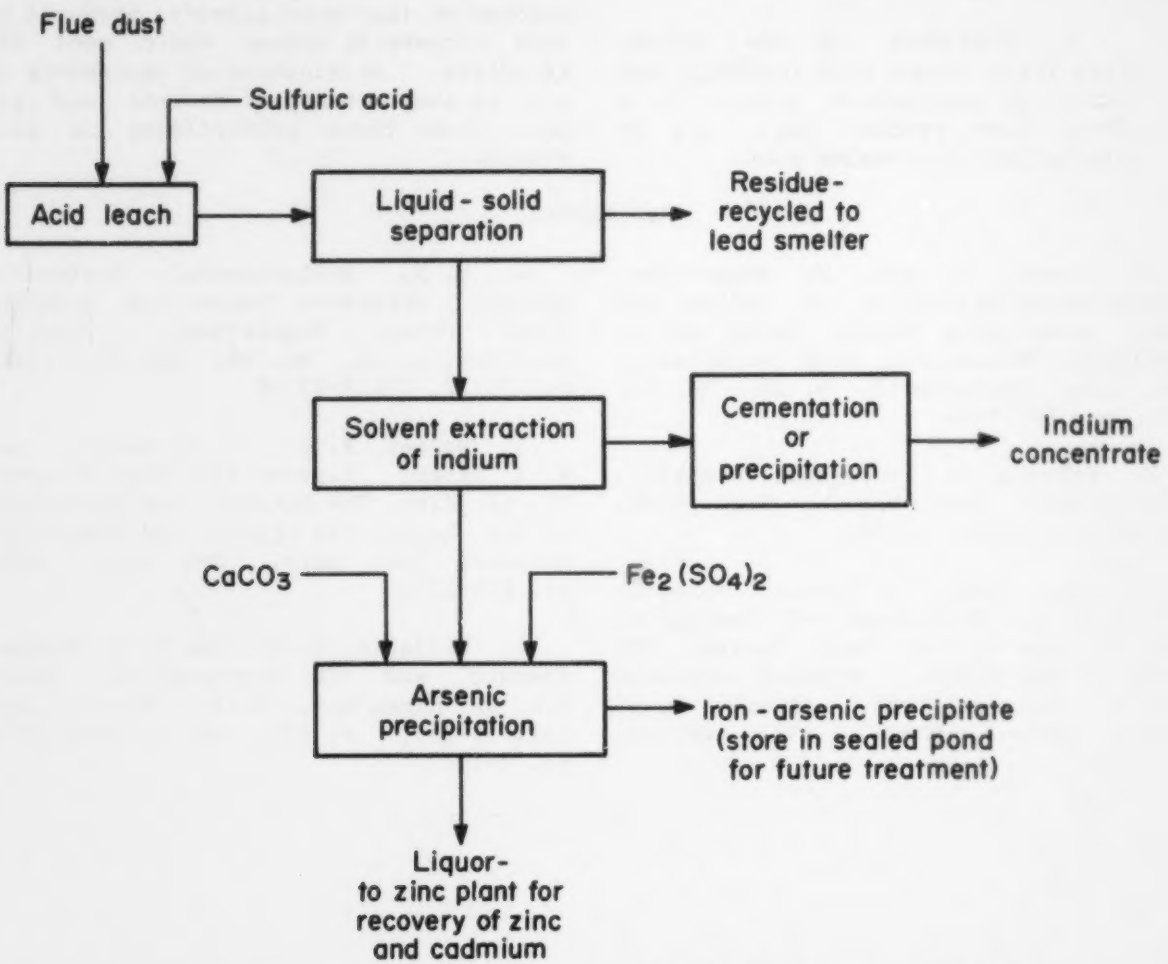

FIGURE 3. - Proposed flowsheet for treatment of lead smelter copper dross flue dust.

CONCLUSIONS AND RECOMMENDATIONS

On the basis of this study, the following conclusions are drawn regarding the treatment of an arsenical flue dust from a lead smelter with an adjoining electrolytic zinc plant:

1. A method is proposed for processing arsenical flue dusts from lead smelters by the following sequence:

   A. H_2SO_4 leaching of the dust to solubilize Zn, As, Cd, and In, and recover a $PbSO_4$ residue that can be recycled back to the smelter.

   B. Treatment of the acid-leach liquor to recover indium by solvent extraction with EHPA.

   C. Treatment of the indium-free leach liquor with $Fe_2(SO_4)_3$ and $CaCO_3$ to precipitate arsenic in a dense form product that can be stockpiled in a sealed pond.

   D. Use of the indium- and arsenic-free solution as makeup in the zinc electrolytic plant, where both zinc and cadmium can be recovered.

2. In an alternative version, step 1B can be eliminated, and an arsenic precipitate containing indium can either be stockpiled or shipped to an outside processor for recovery of arsenic and indium.

More research is needed on a larger scale to demonstrate the feasibility of integrating all of the operations covered in this report. Laboratory research is also needed to develop methods for fixing cadmium so that precipitates produced by this processing scheme would meet EPA standards. Development of technology to aid in the recovery of arsenic and cadmium from these precipitates is also needed.

REFERENCES

1. Cornea, A. and T. Segarceanu. Liquid-Liquid Extraction of Indium and Some Accompanying Metals Using di-(2-ethylhexyl)-Phosphoric Acid as Solvent. Rev. Chim. (Bucharest), v. 15, No. 12, 1964, pp. 723-730.

2. Ephraim, F. Inorganic Chemistry. Interscience Publishers, New York, 6th edition, 1954, p. 76.

3. Mehta, Anil. A Research Investigation of New Techniques for Control of Smelter Arsenic Flue Dust Wastes, EPA Grant R 804595010. Mineral Research Center, Montana Tech. Alumni Foundation, Butte, Mont., 1977, sec. 4, pp. 1-43.

4. U. S. Environmental Protection Agency. Hazardous Waste and Consolidated Permit Regulations. Federal Register, v. 45, No. 98, May 19, 1980, pp. 33122, 33127-33128.

5. Weimer, F. S., G. T. Wevner, and R. J. Lapee. Electrolytic Zinc Process. Ch. in Zinc, The Science and Technology of the Metal, Its Alloys and Compounds. Reinhold Pub. Corp., New York, 1959, pp. 174-225.

6. Whitacre, R. W., and C. S. Pearse. Arsenic and the Environment. Colo. Sch. of Mines Res. Inst. Miner. Ind. Bull. 17(3), v. 17, No. 3, May 1974, pp. 1-19.

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